



Cycling performance and safety of rechargeable lithium cells with binary and ternary mixed solvent electrolytes

S.-I. TOBISHIMA*, K. HAYASHI, Y. NEMOTO and J.-I. YAMAKI

NTT Integrated Information & Energy Systems Research Laboratories, Nippon Telegraph and Telephone Corporation, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1193, Japan

(*author for correspondence, e-mail: tobi@iba.iecl.ntt.co.jp)

Received 15 September 1998; accepted in revised form 5 January 1999

Key words: 2-methyl-tetrahydrofuran, cell safety, ethylene carbonate, lithium cell, organic electrolyte, propylene carbonate

Abstract

The influence of electrolyte composition on the cycling performance and safety of AA rechargeable cells with a lithium metal anode, and an amorphous (a-) V_2O_5 - P_2O_5 cathode was examined. The cells were cycled at a discharge current of 1000 mA and a charging current of 200 mA. The electrolytes were composed of ethylene carbonate (EC)/2-methyltetrahydrofuran (2MeTHF) binary and EC/propylene carbonate (PC)/2MeTHF ternary mixed solvents containing 40–70 vol % 2MeTHF to provide higher conductivity. The solute was 1.5 mol dm^{-3} $LiAsF_6$. The cycle life of the AA cells was evaluated by setting the end of cycle life at the cycle number where the discharge capacity fell to 50% of its maximum value. Cells with EC/2MeTHF (50:50) exhibited the longest cycle life among all the electrolytes examined here. Cells with EC/PC/2MeTHF (15:45:40) had the longest cycle life among the ternary mixed solvents systems. Fundamental abuse tests were also carried out on AA cells, which were cycled twice (fresh cells), cycled 100 times and cycled until the end of their cycle life. Neither the fresh nor the cycled cells with EC/PC/2MeTHF (15:45:40) smoked nor ignited in a 150°C heating test or in an external short circuit test. However, the fresh cell with EC/2MeTHF (50:50) ignited in the 150°C heating test. Summarizing the cycling and the abuse test results, the EC/PC/2MeTHF (15:45:40) ternary mixed systems exhibited the best performance. However, in terms of practical use, cell safety still requires further improvement.

1. Introduction

Rechargeable cells with lithium metal anodes are attractive because theoretically they have a higher energy density than lithium ion cells with lithium ion doped carbon anodes. With the lithium metal cell system, the most important problems to be solved are those related to cycle life, rate capability and safety. These problems are closely related to the selection of a suitable electrolyte [1–4].

We have been studying rechargeable cells with a lithium (Li) metal anode, an amorphous (a-) V_2O_5 - P_2O_5 (95:5 in molar ratio) cathode and nonaqueous electrolytes (Li/a- V_2O_5 - P_2O_5 cell). We have reported that $LiAsF_6$ -ethylene carbonate (EC)/propylene carbonate (PC)/2-methyltetrahydrofuran (2MeTHF) (15:70:15 in volume mixing ratio) (type-A electrolyte) provides a

long cycle life which ensures the safety of AA Li/a- V_2O_5 - P_2O_5 cells [5, 6]. In these studies, the cells were cycled at 600 mA ($\sim 3 \text{ mA cm}^{-2}$) and 100 mA ($\sim 0.5 \text{ mA cm}^{-2}$). However, the type-A electrolyte provides a poor rate capability because of its low electrolyte conductivity [7]. For example, the discharge capacity of the AA Li/a- V_2O_5 - P_2O_5 cell with type-A electrolyte at a discharge current of 1000 mA at 21°C is 50% that at a discharge current of 600 mA. A higher discharge and charge rate capability is required for practical cell applications.

In this work, we examine the cycling performance and safety of lithium metal cells at high discharge and charge rates. The AA Li/a- V_2O_5 - P_2O_5 cells were cycled at a discharge current of 1000 mA and a charging current of 200 mA. The electrolytes were composed of EC/2MeTHF binary and EC/PC/2MeTHF ternary mixed

solvents with a high 2MeTHF content of 40 to 70 vol % to provide high electrolyte conductivity. 1.5 mol dm^{-3} (M) LiAsF_6 was used as the solute. We also carried out fundamental abuse tests including heating and external short circuit tests on the AA lithium metal cells.

2. Experimental details

2.1. Electrolytes

We prepared the electrolyte solutions as described in previous papers [1–4, 6]. Their water content was less than 20 ppm. Hereafter, ‘1.5 M LiAsF_6 -EC/PC/2MeTHF (15:45:40)’ will be used to indicate an electrolyte solution of mixed EC, PC and 2MeTHF solvents (volume ratio 15:45:40). We measured the electrolyte conductivity at 1 kHz with an LCR bridge (Gen Rad Co., model 1658). Solvent viscosity and dielectric constant were obtained according to the methods described in reference [3].

2.2. Charge–discharge cycling efficiency of lithium

Charge–discharge cycling tests for lithium on a stainless steel (SUS 304) working electrode (cathode case of a coin cell) were performed galvanostatically with a coin cell (23 mm in diameter and 2 mm thick) to obtain the lithium cycling efficiency itself [5]. In these experiments, lithium was plated on stainless steel without any excess lithium being deposited. The cycling efficiency was obtained from the stripping charge (Q_s)/plating charge (Q_p) by using the 1.5 V potential cut-off as the stripping end point [4]. We used the average cycling efficiency (E_a) from the first to the 20th cycle for the evaluation, where Q_p was 1 mA h (0.5 mA h cm^{-2}) and the charge–discharge (plating stripping) current density (I_{ps}) was 1 mA (0.5 mA cm^{-2}).

2.3. Fabrication of $\text{Li/a-V}_2\text{O}_5\text{-P}_2\text{O}_5$ cell

The cell used was an AA-size laboratory-type cell with a pressure vent at the top surface of its crimp-sealed casing [8]. This cell was composed of a spirally wound lithium metal anode sheet, a polyethylene separator, a printed cathode sheet of $\text{a-V}_2\text{O}_5\text{-P}_2\text{O}_5$, polymer binder and conductive carbon. $\text{a-V}_2\text{O}_5\text{-P}_2\text{O}_5$ (95 mol % V_2O_5) was prepared by melting reagent-grade oxides in platinum crucibles for an hour at 750°C , followed by quenching on a water-cooled iron block [8]. The charge–discharge cycling tests for the AA cells were carried out galvanostatically with a charge cut-off voltage of 3.3 V

and a discharge cut-off of 1.4 V with a charging current of 200 mA and a discharge current of 1000 mA. The operating temperature of the cell was 21°C unless otherwise noted. The cycle life of the AA cells was evaluated from the cycle numbers or from the figure of merit (FOM) defined in Equation 1 [9], and by setting the end of cycle life (ECL) at the cycle number where the discharge capacity fell to 50% of its maximum value. The figure of merit (FOM) is related to the percentage lithium cycling efficiency (E) as shown in Equation 2.

$$\text{FOM} = \frac{\text{accumulated discharge capacity}}{\text{theoretical capacity of lithium initially put into the cell}} \quad (1)$$

$$\text{FOM} = \frac{100}{100 - E} \quad (2)$$

2.4. Abuse tests

Heating tests were carried out by placing the cells in an incubator. First, the temperature was raised from room temperature to the set level at a rate of 5°C min^{-1} . Then, the temperature was held constant at 150°C for 30 min. External short circuit tests on the cells were carried out through a $30 \text{ m}\Omega$ resistance.

3. Results and discussion

3.1. Electrolyte conductivity

EC and PC are esters with high dielectric constant which are effective for the ionic dissociation of electrolyte salts [5]. 2MeTHF is a low viscosity ether which facilitates ion migration and has a stronger solvation power toward Li^+ ions than EC and PC, as predicted from the donor numbers (DN) of these solvents [10].

Figure 1 shows the relationship between the specific electrolyte conductivity (κ) at 25°C , 0°C and -10°C and the 2MeTHF content in EC/2MeTHF binary mixed solvent electrolytes. At 25°C , the conductivity exhibits a maximum (κ_{max}) at an EC/2MeTHF mixing ratio of 40:60. The reason for this is given below. Figure 2 shows the relationship between the 2MeTHF content, the dielectric constant (ϵ), and the inverse viscosity ($1/\eta$) for the mixed solvents. κ_{max} is the result of the total effect of the dielectric constant and the viscosity [1]. As the temperature is reduced, the κ of the EC/2MeTHF electrolytes containing large amounts of 2MeTHF, such as EC/2MeTHF = 30:70 or 20:80 becomes larger than that of EC/2MeTHF (40:60), and the EC content exhibiting κ_{max} tends to decrease.

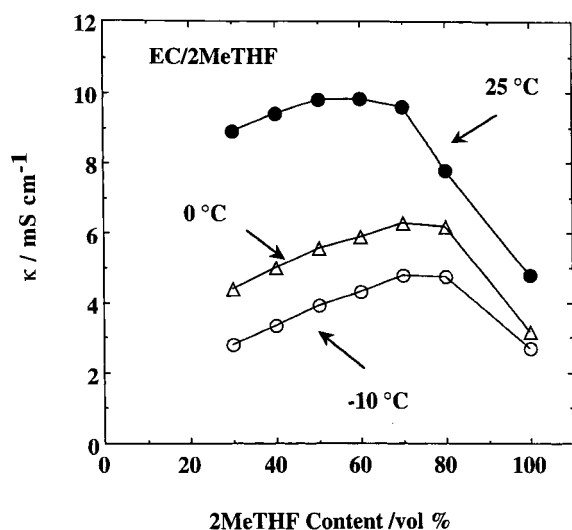


Fig. 1. Relationship between electrolyte conductivity (κ), temperature and 2MeTHF content in 1.5 M LiAsF₆-EC/2MeTHF.

Figure 3 shows the relationship between κ at 25, 0 and -10°C and the 2MeTHF content in EC/PC/2MeTHF ternary mixed solvent electrolytes. At 25°C , the conductivity reaches the κ_{max} at a 2MeTHF content of 60 vol %. The maximum conductivity of EC/PC/2MeTHF is slightly lower than that of EC/2MeTHF with the same 2MeTHF content. Table 1 shows the κ value at 25°C for EC/2MeTHF (40:60) and EC/PC/2MeTHF (15:25:60) along with that of type A electrolyte as a reference electrolyte. EC/2MeTHF (40:60) and EC/PC/2MeTHF (15:25:60) exhibits 47% and 42% higher conductivity than type A electrolyte, respectively. The κ value of the EC/2MeTHF binary mixed solvent electrolyte at 25°C is 9.8 mS cm^{-1} , which is 3% higher than that (9.54 mS cm^{-1}) of EC/PC/2MeTHF ternary mixed solvent electrolyte.

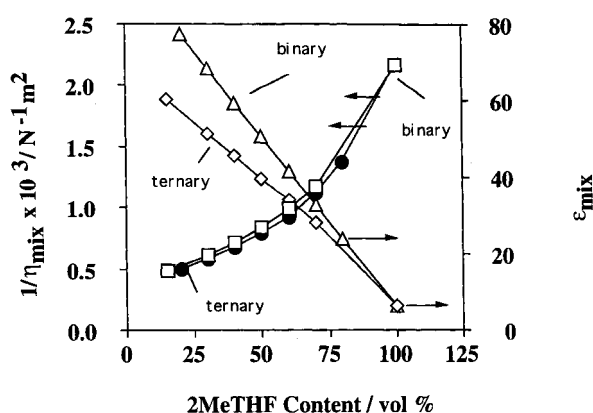


Fig. 2. Relationship between the inverse solvent viscosity ($1/\eta$), the dielectric constant (ϵ) and the 2MeTHF content in EC/2MeTHF and EC/PC/2MeTHF mixed solvents.

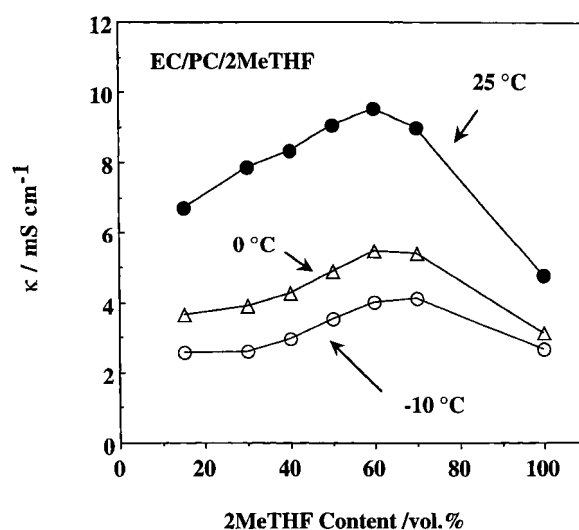


Fig. 3. Relationships between electrolyte conductivity (κ), temperature and 2MeTHF content in 1.5 M LiAsF₆-EC/PC/2MeTHF.

As shown in Figure 4, the activation energy (E_A) obtained from the Arrhenius plot [13] decreases with an increase in 2MeTHF in mixed solvents. The E_A of EC/PC/2MeTHF is smaller than that of EC/2MeTHF, because the order of E_A increase with a change in temperature is EC > PC > 2MeTHF. The higher E_A of EC is caused by the higher melting point of EC (36.2°C).

Based on the above conductivity results, we decided to test EC/2MeTHF and EC/PC/2MeTHF ternary mixed solvent electrolytes containing 2MeTHF from 40 vol % to 70 vol % for the AA Li/a-V₂O₅-P₂O₅ cells to obtain high discharge and charge currents. This is because these electrolyte compositions exhibit conductivities which is much higher than that of type A electrolyte [EC/PC/2MeTHF (15:70:15)].

3.4. Lithium cycling efficiency

Figure 5 shows example results for lithium cycling tests on a stainless steel working electrode. These experiments were carried out to obtain simply the lithium cycling efficiency, not the full cell cycling efficiency. Figure 6

Table 1. Conductivity parameters of the mixed solvent electrolytes at 25°C (1.5 M LiAsF₆)

Solvents	κ /mS cm ⁻¹	ϵ	$\eta \times 10^3$ /N m ⁻¹
EC/PC/2MeTHF(15:25:60)	9.54	34.1	1.01
EC/2MeTHF(40:60)	9.83	41.8	1.08
EC/PC/2MeTHF(15:70:15)*	6.70	60.3	2.06

* 1.15 M LiAsF₆

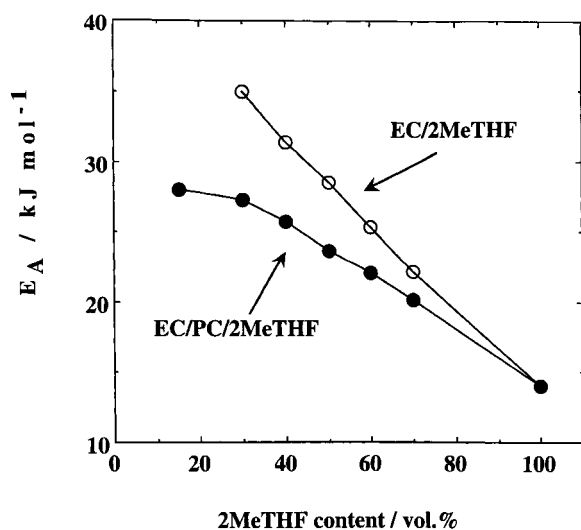


Fig. 4. Relationship between the activation energy (E_A) and 2MeTHF content in 1.5 M LiAsF_6 -EC/2MeTHF and EC/PC/2MeTHF mixed solvent electrolytes.

shows the relationship between 2MeTHF content and the average cycling efficiency (E_a) from the first to the 20th cycle for EC/2MeTHF binary and EC/PC/2MeTHF ternary mixed systems. E_a exhibits its maximum value at EC/2MeTHF = 50:50 for EC/2MeTHF binary and at EC/PC/2MeTHF = 15:35:50 for EC/PC/2MeTHF ternary mixed systems. The binary mixed systems tend to have slightly higher E_a values than ternary mixed systems containing the same amount of 2MeTHF.

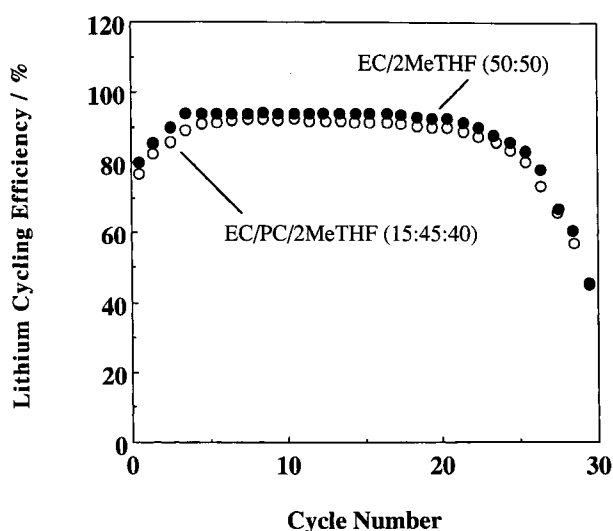


Fig. 5. Relationship between lithium cycling efficiency and cycle number in 1.5 M LiAsF_6 -EC/2MeTHF and EC/PC/2MeTHF mixed solvent electrolytes. $Q_p = 0.5 \text{ mA h cm}^{-2}$, $I_{ps} = 0.5 \text{ mA cm}^{-2}$. Stainless steel working electrode: (●) EC/2MeTHF(50:50) and (○) EC/PC/2MeTHF(15:45:40).

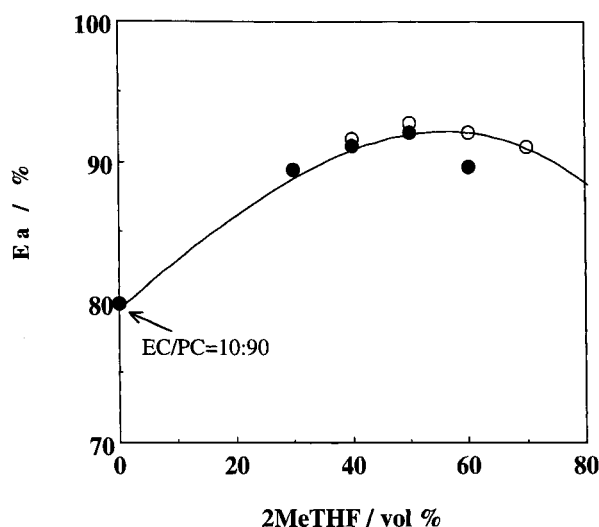


Fig. 6. Relationship between average lithium cycling efficiency (E_a) and 2MeTHF content in 1.5 M LiAsF_6 -EC/2MeTHF and EC/PC/2MeTHF mixed solvent electrolytes, $Q_p = 0.5 \text{ mA h cm}^{-2}$, $I_{ps} = 0.5 \text{ mA cm}^{-2}$. Stainless steel working electrode: (○) EC/2MeTHF binary and (●) EC/PC/2MeTHF ternary mixed solvents.

Lithium cycling efficiency is affected by many factors, such as the reactivity of the electrolyte toward lithium, the chemical and physical properties of the lithium surface film and the lithium deposition morphology [1–4]. These factors are closely related to each other. EC and PC have a similar chemical structure and reactivity. EC is more reactive toward lithium than PC [14]. However, when EC and PC are mixed, the lithium cycling efficiency becomes much greater than that with PC alone [1–4]. This is reported to be due to the slight difference between the chemical compositions of lithium surface film with EC and PC [15]. That is, $\text{CH}_3\text{CH}(\text{OCO}_2\text{Li})\text{CH}_2\text{OCO}_2\text{Li}$ and $(\text{CH}_2\text{OCO}_2\text{Li})_2$ are detected in lithium surface film with dry PC and EC, respectively [15]. The difference between the E_a values of EC/2MeTHF and EC/PC/2MeTHF is due to the effect of EC mentioned above.

The addition of small amounts of 2-methylfuran (2MeF), which is an impurity in 2MeTHF, to ether-based electrolytes, such as 2MeTHF and THF, is reported to be a very effective way of improving the lithium cycling efficiency [16]. This is because highly reactive 2MeF produces a suitable lithium surface film for cycling lithium well [17]. The 2MeF content of the 2MeTHF used in this work was 0.06 vol.%, which was less than the amount generally reported (0.2–0.4 vol.%) [18] and was considerably lower than the effective amount for improving lithium cycling efficiency (1.0–2.5 vol.%) [16]. We have found that the lithium cycling efficiency in EC/2MeTHF depends greatly on purity and

the cycling efficiency increases with a reduction in organic impurities [19]. The effect of adding 2MeF to highly pure EC/2MeTHF was negligible [19]. Therefore, the reactivity of EC itself rather than 2MeF may affect the lithium cycling efficiency via the production of suitable surface film. With $\text{LiAsF}_6\text{-EC/PC/2MeTHF}$ and EC/2MeTHF, the possible main chemical components in the lithium surface film are lithium alkoxide formed from 2MeTHF, lithium alkyl carbonates and lithium carbonate formed from EC and PC, LiF and lithium arsenic fluorides formed from LiAsF_6 [20]. The deepest compact layer in the surface film in EC/2MeTHF (50:50) exhibiting the highest E_a is considered to be a good lithium ion conductor leading to both high lithium cycling efficiency and a smooth lithium deposition morphology [1–4].

When the same solvents are used, the cycling efficiency is known to vary with the electrolyte composition [1–4, 11]. However, the reason for achieving maximum efficiency with a change in the electrolyte composition is very hard to explain theoretically although the chemical composition and properties of the surface film seem to change when the electrolyte composition is changed. Thus, the easiest way is to measure the lithium cycling efficiency to obtain the best electrolyte composition with the various mixed solvent systems. As the reproducibility of the data shown in Figures 6 and 7 is good, we can conclude that the highest lithium cycling efficiency is obtained at EC/2MeTHF = 50:50 in the binary and EC/PC/2MeTHF = 15:35:50 in the ternary mixed solvent electrolytes examined here.

3.5. Cycling tests on AA Li/a- V_2O_5 cells with mixed solvent electrolytes

The cell capacity of AA Li/a- $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ cell used in this work at a discharge current of 1000 mA is approximately 800 mA h. For this cell, the charging current of 200 mA is approximately equal to the 4 h charge rate. With lithium metal cells, a high rate charge is difficult because the lithium deposition morphology tends to be needle like [21]. Then, a 0.1 C rate (10 h charge rate) is frequently used [22]. The charge rate used in this work is considered to be a quick charge [23], completing the within 5 h.

Figures 7 and 8 show the cycling test results for the AA Li/a- $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ cells with EC/2MeTHF binary and with EC/PC/2MeTHF ternary mixed solvent electrolytes cycled at 1000 mA discharge and 200 mA charge currents between 1.4 and 3.3 V, respectively. Figure 9 shows the relationship between the 2MeTHF content and figure of merit (FOM) of AA cells with EC/2MeTHF binary mixed solvent electrolytes. The maxi-

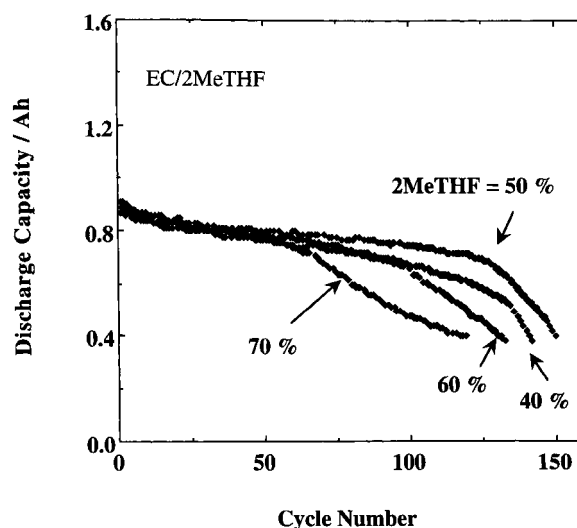


Fig. 7. Cycling test results for an AA Li/a- $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ cell with 1.5 M $\text{LiAsF}_6\text{-EC/2MeTHF}$ binary mixed solvent electrolytes cycled at 1000 mA discharge and 200 mA charge currents between 1.4 and 3.3 V.

um FOM is obtained at EC/2MeTHF = 50:50. This result tends to coincide with the lithium cycling efficiency. Figure 9 also shows the relationship between the 2MeTHF content and FOM of AA cells with EC/PC/2MeTHF ternary mixed solvent electrolytes. The maximum FOM is obtained at EC/PC/2MeTHF = 15:45:40, although lithium cycling efficiency is obtained at EC/PC/2MeTHF = 15:35:50. This difference arises

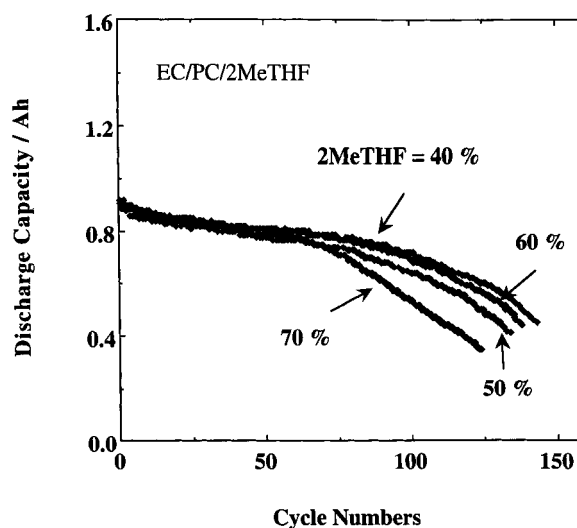


Fig. 8. Cycling test results for an AA Li/a- $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ cell with 1.5 M $\text{LiAsF}_6\text{-EC/PC/2MeTHF}$ ternary mixed solvent electrolytes cycled at 1000 mA discharge and 200 mA charge currents between 1.4 and 3.3 V.

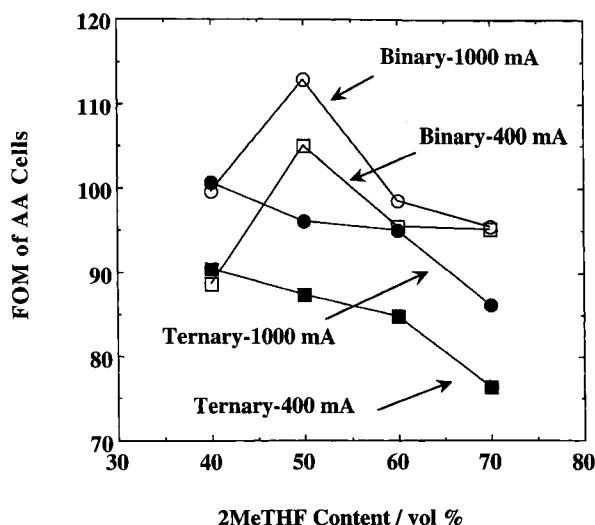


Fig. 9. Relationship between the FOM of an AA Li/a- V_2O_5 - P_2O_5 cell and 2MeTHF content in 1.5 M LiAsF₆-EC/2MeTHF and EC/PC/2MeTHF mixed solvent electrolytes cycled between 1.4 and 3.3 V.

from the EC/PC mixing ratio. Studies have already been undertaken on the EC interaction with amorphous V_2O_5 and the cycle life of Li/a- V_2O_5 full cell that decreases with an increase in the EC content of an EC/PC mixture, while the lithium cycling efficiency increases with an increase in EC content [24]. The FOM of the cells with binary mixed electrolytes tends to be larger than that with ternary mixed electrolytes. These results generally agree with those of lithium cycling efficiency.

As a reference, the cycling tests were performed on the cells with a low discharge current of 400 mA and the same charge current of 200 mA as for those mentioned above. As shown in Figure 9, the FOM of the cells with a 400 mA discharge was lower than that with 1000 mA for both binary and ternary mixed electrolytes. This result is common to the lithium metal cells [22]. This is because the lithium deposition morphology becomes mossy and electrochemically inert lithium is increased by the exfoliation of lithium from the anode and the increase in the surface area of the deposited lithium causes an increase in reactivity [25]. In 400 mA discharge cycles, the binary mixed electrolytes also tend to show a larger FOM than those with ternary mixed electrolytes. The best FOM is obtained with an EC/2MeTHF = 50:50 and the second best FOM is obtained with EC/PC/2MeTHF (15:45:40). These results coincide with those for 1000 mA discharge cycles. Thus, we believe that the FOM of the cells under the cycling conditions mentioned above is determined mainly by the lithium anode cycling efficiency.

The above cycling test results show that EC/PC/2MeTHF (15:45:40) ternary and EC/2MeTHF (50:50)

binary mixed solvent electrolytes perform better than the others. However, possible problems remain in terms of cell safety.

3.6. Abuse test results

Thermal runaway is a basic problem as regards cell safety. When thermal runaway occurs in a lithium metal cell, the cell ignites [8]. Several exothermic reactions occur inside a cell as its temperature increases [8].

It is effective to set the heating temperature above the melting point of the separator as this leads to an internal short between the cathode and anode. In this work, the heating tests were carried out at 150 °C, based on the UL standard procedure (a safety standard for lithium batteries, UL 1642, Underwriters Laboratories Inc., 3rd edn., 1995). 150 °C is sufficiently high for evaluating the thermal stability of the cells because the cells fabricated here have a polyethylene separator whose melting point is 125 °C. In our heating test, the heating temperature is held for 30 min, which is 20 min longer than the UL standard. It is reported that thermal stability depends greatly on the discharge and charge current [26–29]. Also, the thermal stability of lithium metal cells decreases with an increase in charge current and decrease in discharge current. It is also reported that the thermal stability decreases with increases in cycle number. One example of the thermal stability of an AA lithium metal cell reports a temperature of 110 °C, which is the highest heating temperature at which the cell does not ignite [26–29]. It is considered to be very difficult for AA lithium metal cells to pass the 150 °C heating barrier.

Here, we carried out the heating tests on AA cells with EC/PC/2MeTHF ternary and EC/2MeTHF binary mixed solvent electrolytes. Before the heating tests, these cells were cycled twice (fresh cell), 100 times and to the end of cycle life (ECL) at 1000 mA discharge and 200 mA charge currents between 1.4 and 3.3 V. Two cells were tested for each abuse test. Table 2 summarizes the heating test results for AA cells with EC/2MeTHF and EC/PC/2MeTHF electrolytes containing 40–70% 2MeTHF. All the fresh cells ignited except for those with EC/PC/2MeTHF (15:45:40) (Figure 10) and those with EC/PC/2MeTHF (15:35:50). As the 2MeTHF content was decreased, the thermal stability of the AA cells tended to increase. The cell with EC/2MeTHF (30:70) had already ignited at 148 °C, as the cell temperature was increased toward 150 °C. One of the reasons for this phenomenon is the low thermal decomposition temperature of 2MeTHF coupled with LiAsF₆, which is exothermic reaction. It starts to decompose at 130 °C [30]. The thermal stability of the cells with

Table 2. Heating test results for AA Li/a-V₂O₅-P₂O₅ cells with 1.5 M LiAsF₆-EC/2MeTHF and -EC/PC/2MeTHF

Solvent vol %			Heating test results		
2MeTHF	EC	PC	Fresh cell	Cell cycled 100 times	Cell cycled at ECL (cycle number)
70	30	–	F	F	F (116)
70	15	15	F	F	F (105)
60	15	25	F	F	F (131)
50	50		F	NF	NF (148)
50	15	35	F	NF	F (121)
40	15	45	NF	NF	NF (134)

F: fire, NF: no fire

ternary mixed electrolytes is better than those with EC/2MeTHF binary mixed electrolytes. Fresh cells with EC/2MeTHF (50:50) ignited at 148 °C, although they showed the best cycle life. The fresh cells and the cells cycled 100 times and to the ECL with EC/PC/2MeTHF (15:45:40) did not ignite. The cells with EC/2MeTHF (50:50) also did not ignite after cycling. Figure 11 shows the relationship between the maximum cell skin temperature and cycle number. At the ECL, the cell with EC/PC/2MeTHF (15:45:40) exhibited a maximum cell temperature of 154 °C (4 °C increase by the internal heat output). However, the cell with EC/2MeTHF (50:50) showed a maximum temperature of 175 °C, which is close to the melting point of lithium (180 °C) and about 20 °C higher than that with EC/PC/2MeTHF (15:45:40). That is, the safety margin of the cell with EC/2MeTHF(50:50) is considerably lower than with EC/PC/2MeTHF (15:45:40). The cell with EC/2MeTHF (30:70) containing high amounts of 2MeTHF ignited violently after cycling.

Therefore, the cycling performance and thermal stability of EC/PC/2MeTHF (15:45:40) is the best among the electrolyte systems examined here. However, further improvement is still necessary in the thermal stability before practical use can be considered. This is because when the cells were cycled at a lower discharge current of 400 mA and at the charge current of 200 mA, even the cell with EC/PC/2MeTHF (15:45:40) cycled to its ECL ignited in a 150 °C heating test as shown in Figure 12.

4. Conclusion

The following statements can now be made. (i) A Li/a-V₂O₅-P₂O₅ cell with EC/2MeTHF (50:50) binary

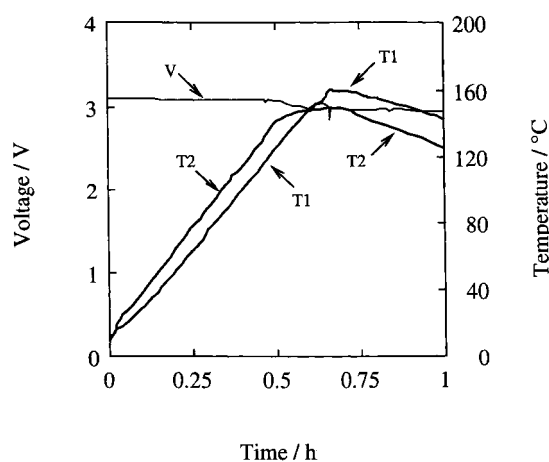


Fig. 10. Heating test results at 150 °C for an AA Li/a-V₂O₅-P₂O₅ fresh cell with 1.5 M LiAsF₆-EC/PC/2MeTHF(15:45:40). Cell skin temperature (T1); oven temperature (T2); cell voltage (V).

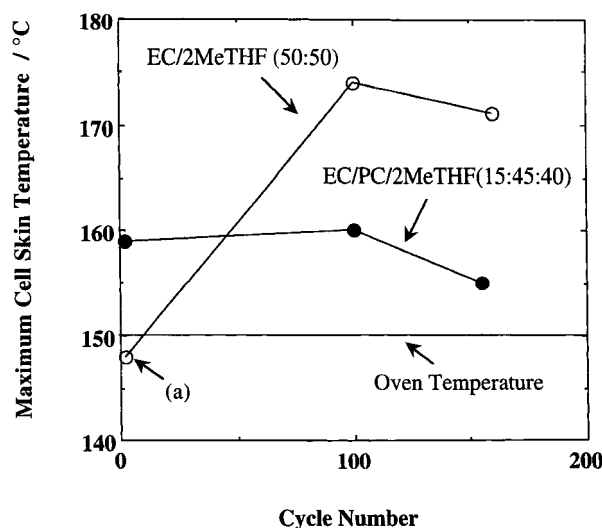


Fig. 11. Relationship between the maximum cell skin temperature in the 150 °C heating test and cycle number for AA Li/a-V₂O₅-P₂O₅ cells with 1.5 M LiAsF₆-EC/2MeTHF and EC/PC/2MeTHF mixed solvent electrolytes cycled at 1000 mA discharge and 200 mA charge currents between 1.4 and 3.3 V, (a) ignited before reaching 150 °C.

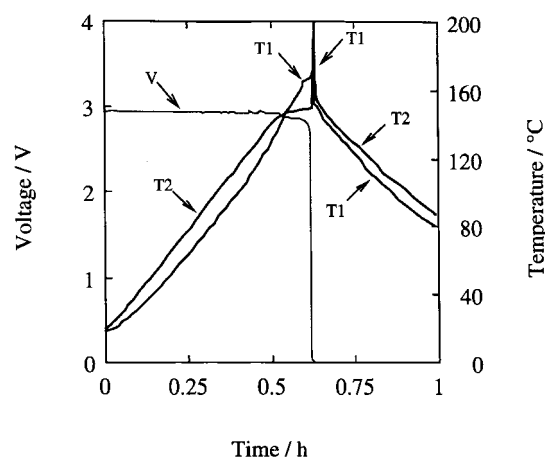


Fig. 12. Heating test results at 150 °C for an AA Li/a-V₂O₅-P₂O₅ cell cycled to its ECL with 1.5 M LiAsF₆-EC/PC/2MeTHF(15:45:40), cycled at 400 mA discharge and 200 mA charge currents between 1.4 and 3.3 V. Cell skin temperature (T1); Oven temperature T2; cell voltage V.

mixed solvent electrolyte has the longest cycle life among all the electrolyte systems examined here. (ii) The cells with EC/PC/2MeTHF (15:45:40) showed the best cycle life among the ternary mixed systems. (iii) EC/PC/2MeTHF (15:45:40) exhibited better abuse test results than those with other electrolytes including EC/2MeTHF (50:50). However, we conclude that further improvement in the cell safety is necessary before these cells can be put to practical use.

References

1. G. Pistoia (ed.), *Industrial Chemistry Library*, vol. 5, *Lithium Batteries*, Elsevier Science, The Netherlands, (1994) chapter 4.
2. M. Salomon, *Abstracts of Eighth International Symposium on Solubility Phenomena*, Niigata, Japan (1998) p. 7.
3. G.P. Gabano (ed.), *Lithium Batteries*, Academic Press, London, chapters 2 and 13. (1983).
4. J.O. Besenhard (ed.), *Handbook of Battery Materials*, Wiley-VCH, Weinheim, (1998) chapter 3.1.
5. S. Tobishima, K. Hayashi, Y. Nemoto and J. Yamaki, *Electrochim. Acta* **42** (1997) 1709.
6. S. Tobishima, K. Hayashi, Y. Nemoto and J. Yamaki, *J. Appl. Electrochem.* **27** (1997) 902.
7. S. Tobishima, K. Hayashi, Y. Nemoto and J. Yamaki, *Electrochim. Acta* **43** (1998) 925.
8. S. Tobishima, Y. Sakurai and J. Yamaki, *J. Power Sources* **68** (1998) 455.
9. K.M. Abraham, J.L. Goldman and D.L. Natwig, *J. Electrochem. Soc.* **129** (1984) 2404.
10. V. Gutman, *The Donor-Acceptor Approach To Molecular Interactions*, Plenum Press, New York (1978) pp. 13-33.
11. S. Tobishima and T. Okada, *Electrochim. Acta* **30** (1985) 1715.
12. M.Z.A. Munshi and B.B. Owens, *Polymer J.* **20** (1988) 577.
13. I.D. Raistrick, C. Ho and R.A. Huggins, *Mat. Res. Bull.* **11** (1986) 953.
14. Y. Ein-Eli, B. Markovsky, D. Aurbach, Y. Carneli, H. Yamin and S. Luski, *Electrochim. Acta* **17** (1994) 2559.
15. D. Aurbach, A. Zaban, Y. Gofer, Y. Ein-Eli, I. Weissman, O. Chusid and O. Abramson, *J. Power Sources* **54** (1995) 76.
16. K.M. Abraham, J.S. Foos and J.L. Goldman, *J. Electrochem. Soc.* **131** (1984) 2197.
17. L.A. Dominey, J.L. Goldman and V.R. Koch, *Proceedings of the symposium on Primary and Secondary Lithium Batteries* vol. 91-3, The Electrochem. Society, Pennington, NJ, (1991) p. 293.
18. J.L. Goldman, R.M. Mank, J.H. Young and V.R. Koch, *J. Electrochem. Soc.* **127** (1980) 1461.
19. J. Yamaki and S. Tobishima, *Proceedings of the symposium on Primary and Secondary Lithium Batteries*, vol. 91-3, The Electrochem. Society, Pennington, NJ, (1991) p. 235.
20. D. Aurbach, A. Zaban, Y. Ein-Eli, I. Weissman, O. Chusid, B. Markovsky, M. Levi, E. Levi, A. Schechter and E. Granot, *J. Power Sources* **68** (1997) 91.
21. M. Arakawa, S. Tobishima, Y. Nemoto, M. Ichimura and J. Yamaki, *J. Power Sources*, **43-44** (1993) 27.
22. F.C. Laman and K. Brandt, *J. Power Sources* **21** (1987) 195.
23. T. Takamura and Y. Sato, *Battery Handbook for Users* (in Japanese), The Institute of Electronics, Information and Communication Engineers, Tokyo, (1988) p. 15.
24. S. Tobishima, K. Hayashi, K. Saito, T. Shodai and J. Yamaki, *Electrochim. Acta*, **42** (1997) 119.
25. K. Saito, M. Arakawa, S. Tobishima and J. Yamaki, *J. Power Sources* **72** (1998) 111.
26. D.P. Wilkinson and J.R. Dahn, *Extended Abstracts of Electrochemical Society, Fall Meeting*, Abstract 53, Seattle, WA, (1990) p. 85.
27. M.W. Juzkow, *Extended Abstracts of Electrochemical Society, Fall Meeting*, Abstract 48, Seattle, WA, (1990) p. 76.
28. U. von Sacken and J.R. Dahn, *Extended Abstracts of Electrochemical Society, Fall Meeting*, Abstract 54, Seattle, WA, (1990) p. 87.
29. L. Lechmer and H. Woo, *Extended Abstracts of Electrochemical Society Fall Meeting*, Abstract 14, Phoenix, AZ, (1991) p. 20.
30. M.A. Gee and F.C. Laman, *J. Electrochem. Soc.* **140** (1993) L53.